Thresholdless antiferroelectricity in liquid crystals and its application to displays

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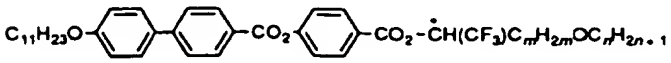
By diminishing the energy barrier between SC_A^* and SC*, antiferroelectricity has become thresholdless in a three-component mixture. It shows V-shaped switching, realizing attractive display characteristics: extremely wide viewing angle with very large contrast ratio, high speed response and ideal analogue grey scale with no hysteresis. A simplified model of the phase with this property is presented.

Ordinary antiferroelectricity in liquid crystals (LCs) shows tristable switching, which is the electric-field-induced transition between antiferroelectric (AF) smectic C_A^* (SC_A^*) and ferroelectric (F) smectic C* (SC*) phases and has characteristic dc threshold and hysteresis.[1] By applying a positive or negative bias field, the tristable switching in AFLCs can be used in a way similar to the bistable switching in FLCs;[2,3] two F states give the same transmittance, so that we can alternately use them symmetrically. This fact assures an extremely wide viewing angle with a relatively large contrast ratio of 30. Since AFLCs have some additional characteristics which make them superior to FLCs, they have received much attention and two prototype AFLC displays using passive matrix (PM) addressing have been developed and exhibited.[4,5] What prevents AFLC displays from achieving much larger contrast ratios is the pretransitional effect in the electric-field-induced AF–F phase transition, which appears as a slight increase in transmittance below the threshold.

During the development of materials to suppress the pretransitional effect, we encountered materials which show a large pretransitional effect and, at the same time, a remarkable decrease in the threshold field strength. Hence we propose that pretransitional-effect enhancement in combination with the use of active matrix (AM) or thin-film transistor (TFT) addressing is another way to endow LCs with attractive display characteristics. The materials here investigated are compounds and their mixtures possessing trifluoroalkoxyalkyl carboxylate groups and partially fluoro-substituted phenyl rings.

In a series of compounds with the general molecular structure **1**



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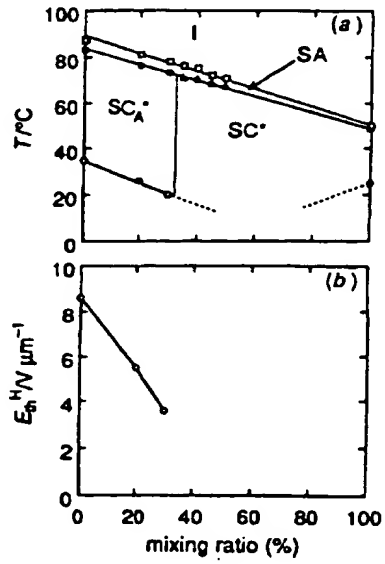
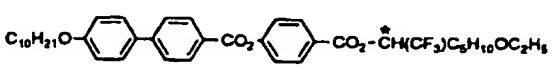
an ether linkage and its position in the chiral end chain were reported to have a subtle influence on the threshold field, E_{th}^H.[6,7] When the ether linkage is located at the chain terminal, E_{th}^H is higher than that of the reference substance of equal chain length but with no ether linkage. As the linkage moves towards the core, E_{th}^H becomes lower and finally F appears instead of AF. Blending further reduces E_{th}^H as illustrated in Fig. 1. Furthermore, the pretransitional effect can be enhanced by suitably substituting the phenyl rings with fluorine. To evaluate the pretransitional effect, we measured the contrast ratio, T_F/T_{AF}, just below E_{th}^H; the smaller the contrast ratio, the larger the pretransitional effect. Table 1 summarizes the results, indicating that Y_1 substitution causes the most marked decrease in the contrast ratio, and hence the greatest increase in the pretransitional effect.

In this way, we can enhance the pretransitional effect and reduce the threshold, E_{th}^H. But can we prepare a system where the threshold becomes zero, so that the pretransitional effect prevails and the AF–F phase transition occurs continuously? Surprisingly, it was not difficult to realize this property, which





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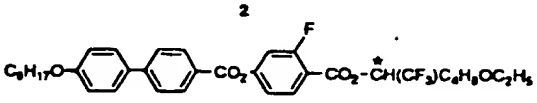

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Fig. 1 Phase diagram of (*a*) the binary mixture system of compounds **2** and **3**, and (*b*) the threshold field *vs.* mixing ratio plot

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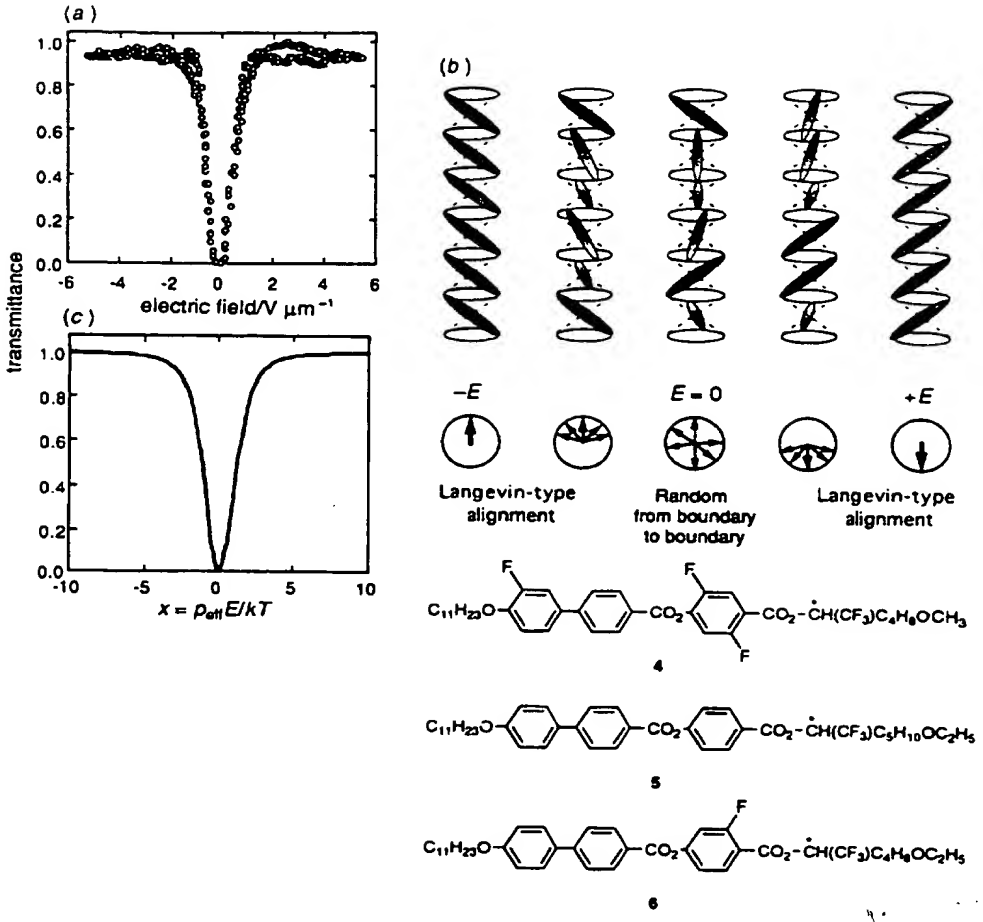
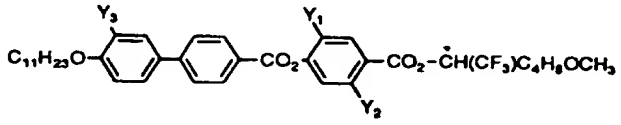


Fig. 2 (*a*) V-shaped switching observed in a three-component mixture of compounds 4, 5 and 6, with the mixing ratio of 4:5:6 = 40:40:20 (mass%). (*b*) Simplified model of the phase with thresholdless antiferroelectricity, SC_R^*. (*c*) Simulated light transmittance as a function of the normalized electric field.

Table 1 Effects of fluoro-substitution at positions Y_1–Y_3 of compound 7 on the contrast ratio



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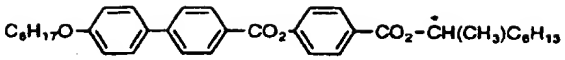
Y_1	Y_2	Y_3	contrast ratio
H	H	H	36
H	F	H	27
F	H	H	12
H	H	F	31
H	F	F	28
F	H	F	10

we designate as 'thresholdless antiferroelectricity'‡ in a three-component mixture, and the field-induced F–AF–F phase transition now appears as V-shaped switching as shown in Fig. 2(*a*). When we observed the switching using a polarizing optical microscope, the visual field varied uniformly and continuously without showing any irregularities indicating the boundary movement characteristic of the tristable switching or the disclination lines caused by the helicoidal unwinding of FLCs. The V-shaped switching is totally different from the tristable switching and the helicoidal unwinding.

Although we have to optimize the V-shaped switching by further developing suitable materials, the properties at 25 °C of the three-component mixture has already realized potentially attractive display characteristics: (i) a tilt angle $>35°$ assuring efficient light transmission in its bright state; (ii) <2 V μm^{-1} for completing F–AF–F switching which makes low-voltage driving possible; (iii) light transmission almost linear to the applied field and free from hysteresis, which produces an ideal analogue grey scale; (iv) <50 μs AF–F switching time; (v) a contrast ratio up to 100; and (vi) an extremely wide viewing angle of $>60°$. None of the currently available FLC and AFLC materials realized displays that possessed all of these characteristics; an analogue grey scale is difficult to achieve with surface-stabilized FLCs with PM addressing,[3] deformed-helix FLCs with AM or TFT addressing is disrupted by hysteresis,[8,9] and AFLCs with PM addressing could not attain very large contrast ratios.[4,5] Only thresholdless antiferroelectric LCs with AM or TFT addressing, as described herein, are considered to possess all of those attractive display characteristics.

Let us consider the thresholdless antiferroelectricity in connection with the molecular rotational motion which plays an essential role for the emergence of in-layer spontaneous polarizations in liquid crystals.[10] Recently, we experimentally confirmed in a prototype AFLC 8

‡ This term is self-contradictory, because going from AF to F requires a symmetry change. However, it is profitable to slightly extend the definition of antiferroelectricity because of the present novel and potentially very interesting observation in liquid crystals. The mechanism by which the net spontaneous polarization is cancelled is randomization, but not the antiparallel arrangement. If we include the randomization mechanism, the AF–F transition may become thresholdless.



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that the hindered rotational motion of the carbonyl group in the chiral end chain is described by the distribution function

$$f(\psi)=(1/2\pi)\{1+a\cos(\psi-\psi_0)\}$$

where ψ is the angle of rotation of the carbonyl about the long molecular axis and a the degree of hindrance; the hindered direction ψ_0 in SC_A^* (ψ_0^{AF}) is substantially different from that in SC* (ψ_0^F).[11] The pretransitional effect may be considered as a slight change in ψ_0, from ψ_0^{AF} towards ψ_0^F. Thus we speculate that in the phase with thresholdless antiferroelectricity, the hindered rotational motions (more generally, the states of the chiral end chain as a whole) characterized by ψ_0^{AF} and ψ_0^F in SC_A^* and SC* have nearly the same energies and furthermore the barrier between them diminishes, so that the states characterized by any ψ_0 between ψ_0^{AF} and ψ_0^F are equally thermally excited at zero electric field; this arbitrary nature of ψ_0 makes the molecular tilting direction non-correlated between adjacent layers. The director tilting is uniform and has constant polar and azimuthal angles in a smectic layer, but its azimuthal angle varies randomly from layer to layer. In-layer spontaneous polarizations exist at smectic-layer boundaries, with random orientations and variable magnitudes from boundary to boundary; hence there is no net spontaneous polarization. We designate the phase with thresholdless antiferroelectricity as SC_R^* with (R = random), § a simplified model of which is shown in Fig. 2(*b*).

An electric field applied perpendicular to the substrate plates along the smectic layer induces a net spontaneous polarization according to the Langevin-type equation.[13] However, it differs from the ordinary Langevin equation in that (1) we are dealing with very large effective dipole moments of variable magnitude owing to the cooperative interaction of many molecules which produce in-layer spontaneous polarizations, and (2) the rotation of the effective dipole moments is restricted in the two-dimensional space. The light transmittance, which is V-shaped as shown in Fig. 2(*c*), was obtained by assuming that the effective dipole moments have the same magnitude, p_{eff}, and follow the same distribution as the *c*-director which can be approximated by an apparent angle, and that the index of ellipsoid is uniaxial with eigenvalues, $n_\parallel = 1.7$ and $n_\perp = 1.5$, which are independent of the field applied. Other parameters used were wavelength $\lambda = 500$ nm, cell thickness $d = 1.7$ μm and molecular tilt angle $\theta = 35°$.

§ Since the macroscopic symmetry of SC_R^* is the same as that of SA, the V-shaped switching could be regarded as an electroclinic effect.[12] In an actual cell, the substrate surfaces impose some restrictions and the azimuthal angle distribution may not be cylindrically symmetrical around the smectic layer normal.

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